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AT SITES FOR UNDERGROUND COAL CONVERSION

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ELECTROCHEMICAL ENGINES FOR POWER GENERATION AND LOAD-LEVELING

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ABSTRACT

The integration of fuel generation by underground processing of coal with commercial consumption of the fuel at the mine site offers highly efficient utilization of energy. Commercial versions of Li/I$_2$ electrochemical engines to be used in one way of integration are postulated, described and evaluated on the basis of laboratory and theoretical studies. These engines are shown to be valuable for electric power generation and storage in connection with underground coal conversion (UCC) in arid land such as Northwestern New Mexico. Such engines, combined with UCC, could convert roughly 26% of the coal energy to electric power while recovering about 22% of the energy as pyrolysis hydrocarbons. The engines also provide load leveling so that peak power generators would be unnecessary.

WATERLESS ELECTRIC POWER GENERATION, power storage, coal gasification, and hydrocarbon synthesis are offered at arid sites. In this example of integrated fuel-generation and power-generation systems. UCC (underground coal conversion) is operated along with Li/I$_2$ electrochemical engines (1-4)* which have been tested in laboratory devices at the Los Alamos Scientific Laboratory. This paper describes the devices and analyzes how commercial models would be expected to perform in the joint functions of generation and load-leveling at a UCC site which also generates pyrolysis products and moderately low-Btu fuel gases.

THE NEED FOR THIS SYSTEM

Water - The Southwestern United States has large coal deposits which could replace the vanishing oil and gas deposits and provide energy for the region from Texas to California. However, much of the shallow and strippable coal is already tied up for large energy projects, and deep mining by conventional means is not satisfactory for any of several reasons involving safety, economics, or environment. To reach the now-unavailable coal, LASL has turned to UCC (underground coal conversion).

For the UCC LASL has sought waterless methods for conversion of the coal to recovered gaseous or liquid fuels. For the long term, such waterless methods are probably the only ones which will be politically acceptable for new projects in the region—new water uses for non-agricultural purposes take land out of farming, and there is a powerful political impact involved in the distribution of water rights.

The commercial products in the LASL concept of UCC are fuel gases and liquid chemical feedstocks from pyrolysis, plus fuel gases of about 250 Btu/SCF from the gasification of the char which remains after the pyrolysis. Under present economic conditions, this latter fuel gas must be consumed essentially on site because it is too low in Btu content to warrant long distance shipping.

But here we meet least a modest impasse because the present coal-fired electric generation stations consume much water. Although water for power generation has been obtained in the past, it will be much more difficult for new plants to obtain the water that would be needed for conventional electric power generation.

Lithium/iodine electrochemical engines, however, would not require this additional water because they would operate as small units in large groups for which air cooling would be simple.

Load-leveling - The hourly variation of electric power usage coupled with an absence of adequate devices for large-scale energy storage has led to both energy-wasteful marketing of electric power and corollary political arguments about the waste.

Along with the ability of Li/I$_2$ electrical engines to generate power from heat, they also offer large scale energy storage for periods up to 48 hrs.

Reliability and Dispersal - As electric power generators in the U.S. have become larger, the impacts of equipment failures and other interruptions have become very great.

Electrochemical engines in generating stations would be operated as small, separate modules which could individually be replaced with only very minor impact on the overall production of the plant.

Also, electrochemical engines use a new concept in energy conversion in which the work product appears _directly_ as electrochemical work—no mechanical action is required except for periodic switching.** As corollary, many problems associated with mechanical wear at high temperatures can be avoided if one turns to electrochemical engines for power generation.

* Number in parentheses designate References at end of paper.
** Auxiliary mechanical actions such as the operation of cooling fans may be used as a convenience, but they are not necessary.

INTEGRATED UCC AND POWER GENERATION

It has long been recognized that the overall efficiency of fuel usage can be increased if the waste heat of industrial fuel comsumption can be turned to low-grade uses such as home and commercial space heating. (Where the industrial process requiring heat is the process of generating electric power, the integrated usage is now sometimes called cogeneration.) A major factor in Sweden's highly efficient fuel usage lies with the fact that waste industrial heat can be delivered to residential areas for reuse.

In a related argument GE-Tempo (5) emphasizes that, from the standpoint of fuel usage efficiency, one should seek to avoid using high-grade heat such as gas fires for low-grade uses such as home heating. Speaking more specifically, one ideally should match the heat needed to the heat source, carrying out a series of processes in which the temperature of the heat drops and the waste heat of one process becomes the heat source of the next process. Of course, the delivery of the heat from one area of need to another can become a major economic and engineering limitation on such fuel usage.

In the power generation field, most power is now generated in single-cycle operations in which the heat is used essentially once, although some heat is recycled by preheating water which must be heated anyway in the boilers. It is widely emphasized that present steam turbine systems achieve less than 40%-efficient heat usage, and more efficient multiple-cycle operation are sought, e.g., topping steam turbine operations by first using the high-temperature heat of fuel combustion to drive high-temperature gas turbines, then using the rejected gas turbine heat to operate steam turbines.

It has been pointed out (e.g., 6,7), but is not widely recognized, that integrating power generation with UCC can do much to increase the overall efficiency of fuel usage. Here one ideally will choose a high temperature generator and will use the rejected generator heat to perform underground processes. Here the rejected heat replaces coal combustion which would have been needed if rejected heat were not used. As a consequence multiple cycles, including the use of steam-electric generators, will not be necessary at UCC sites.

Several high temperature generation schemes are on the horizon including high temperature gas turbines, MHD, high temperature fuel cells, high temperature electrochemical engines (8), and potassium-vapor turbines. Some of these schemes when combined with the UCC to utilize rejected heat, could lead to efficiencies well over 50%. Perhaps most promising are the high-temperature fuel cells burning UCC fuel gases of 100-250 Btu/SCF. However, none of these systems are operable because of unsolved problems such as hot gas cleanup to remove SO_2/SO_3, NO_y, and particulates.

Because of the many problems with these new schemes just mentioned, LASL has turned to existing technology (i.e., low-temperature technology) for its present integrated UCC/electric power generation concept. This decision lowers the potential efficiency, but it gains in the likelihood of process success in the near future.

Before turning to the ramifications of this decision, we will discuss a lower-temperature

electrochemical engine for which the gas cleanup will be accomplished by conventional means and for which the materials problems will be less difficult than for the very high-temperature devices.

THE CONCEPT OF ELECTROCHEMICAL ENGINES

Electrochemical engines are both electric power generators and batteries--changing from generation to storage is a simple switching operation. As generators they utilize a limited conversion of heat to work to assist the charging of special batteries so that the charging voltage can be smaller than the discharging voltage.

The emf gain just mentioned can be effected (a) by constructing cells and cell stacks (batteries) whose discharge and recharge reactions involve the consumption and regeneration of a condensible gas, and (b) by attaching a condenser to each cell stack so that control of the condenser temperature can be used also to control the gas pressure and thereby the emf of the cell and battery reactions.

(Thermodynamic analyses of these electrochemical engines are given in the Appendix.)

For our present calculations we will consider electrochemical engines in which lithium metal reacts with gaseous iodine. Two separate, sealed, and evacuated stacks of 100 electrochemical cells will be used to make up one electrochemical engine. Within either stack, if the condenser temperature and the cell stack temperature are both 625 K, the iodine gas pressure is high and the voltage of that stack is 272 V. When the condenser temperature is 298 K and the cell stack temperature is 625 K, then the iodine gas pressure is low and the open circuit voltage is 243 V. (Mutually consistent theoretical and measured results supporting these values are given in the Appendix.)

If these two cell stacks are connected in electrical opposition, positive to positive, with one stack at 272 V and the other at 243 V, then 29 V can be delivered from the negative electrode to an external load. Upon draining at low current (near thermodynamic equilibrium), the 272 V cell stack will drain, but the 243 V cell stack will charge simultaneously. The discharge at 272 V is started with that cell stack fully charged and with the 243 V cell stack fully discharged. When the 272 V stack has discharged, and the 243 V stack has simultaneously been fully charged, then the condenser roles are reversed--the hot condenser (272 V side) is cooled, and the cool condenser (243 V side) is heated. Now current will again flow but with a different direction which can be oriented for the external load by external switching.

In this process there is no net consumption of the electrochemical reactants in the cells, but heat must be supplied--some of this heat at 625 K is converted to electrical power, and other heat is degraded from 625 K to 298 K.

A POSTULATED COMMERCIAL Li/I$_2$ ELECTROCHEMICAL ENGINE

Consistent with the thermodynamic and kinetic information presented in the Appendix, we have designed (but not produced) an electrochemical engine which would perform in a commercially competitive manner.

The Cell Design - Fig. 1 is a promising cell design suitable for mass production. Five different types of solid parts are shown. Electrolyte

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will be add-d after assembly into cell-stack units; the liquid and gaseous cell reactants will be formed at the generating station by electrolysis. Consequently handling and shipping of hazardous chemicals (lithium metal and molecular iodine) will be eliminated.
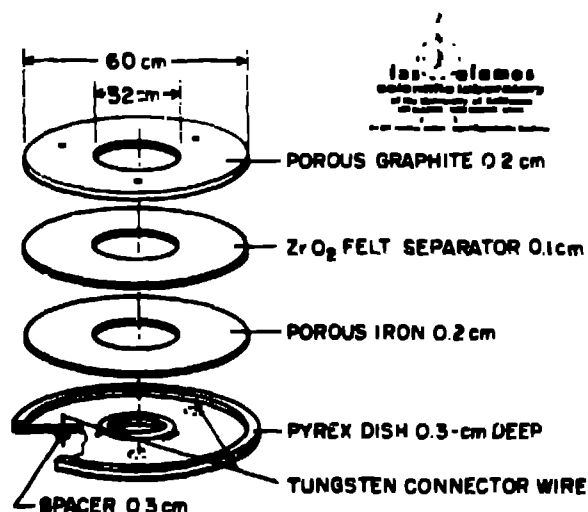

Fig. 1 - Postulated commercial design of Li/I_2 electrochemical engine cells.

The parts of this cell are analogous to those discussed in the Appendix, but the design has been modified to optimize the performance. (A) The cells have been widened and thinned to give 2000 cm^2 working area and to allow many cells to be put into each cell-stack. (B) The tungsten connectors are now rods. They extend 0.5 cm below the bottom of the Pyrex cup in which they are sealed, thereby both providing an electrical connection to the cell below and acting as spacers to open a path for vapor transport. (C) A central hole has been introduced in the cells so that the condenser can be very close to the vapor path from the cells yet radiative losses to the condenser from the cell edges will be small compared to the total process heat transferred.

The Cell-Stack Unit - One hundred cells (Fig. 2) are stacked in a double cylindrical container made from protected steel. The cells touch the outer cylinder, but the inside cylinder (25 cm OD) is smaller than the holes in the cells (30 cm ID). This construction allows heat to be supplied to the outside region while the inside region serves as a condenser, and the space between the cells and the condenser presents unrestricted vapor paths. An open region below the cells serves as the I_2 reservoir.

When the construction of the cell-stack unit is essentially complete, the unit is dipped into a bath of molten electrolyte, then drained, thereby filling the cells with electrolyte. Note that this method of construction and loading allows the cells and cell-stacks to be mass produced, and handling of the hygroscopic electrolyte is minimized.
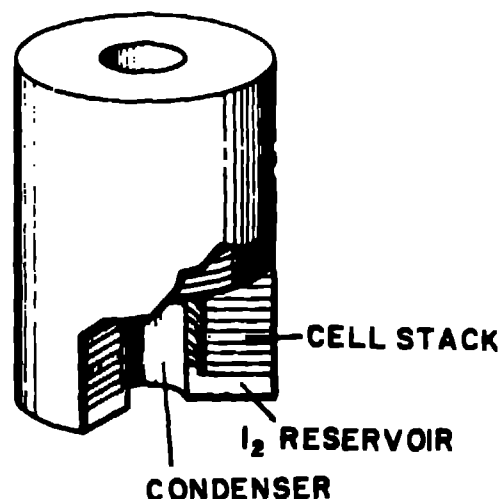

Fig. 2 - One cell-stack unit of an Li/I_2 electrochemical engine showing the cell-stack, condenser, and I_2 reservoir. OD 60 cm, ID 25 cm.

Finally the cell-stack units are evacuated and sealed. Once sealed, a cell-stack unit is not opened again.

The Li/I_2 Electrochemical Engine Design - An electrochemical engine unit is shown in Fig. 3. Two or more such units are operated in electrochemical opposition as is discussed for the laboratory engine model in the Appendix.
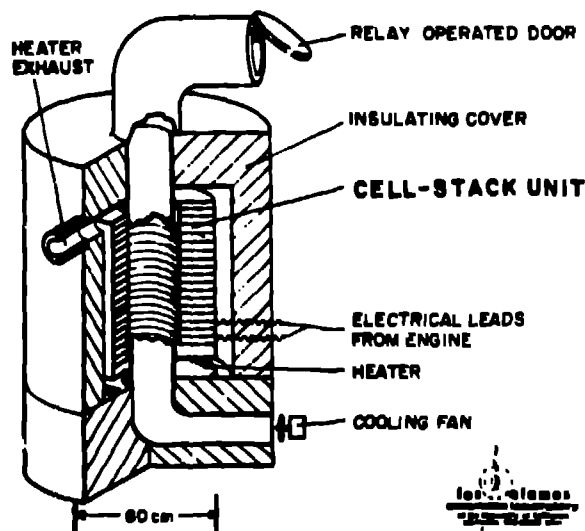

Fig. 3 - Li/I_2 electrochemical engine unit. (Two or more such units make up an electrochemical engine.)

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For operating with UCC the heat will be supplied either as sensible heat or through combustion. Cooling will be by ambient air--if water is available a small amount of cooling of the air by water wick might be used in hot weather.

Anticipated Engine Performance - Consistent with thermodynamic calculations, with experimental performance (see Appendix) for charge and discharge, and with estimated effects of concentration changes as the engines are cycled, we anticipate that engines will operate as is indicated in Table 1.

Table 1 - Performance estimates for proposed Li/I$_2$ electrochemical engines.

One Engine - Two Cell-Stack Units

Cells 2 x 100	200
Cell area each cell	2000 cm^2
Specific resistance	0.8 ohm cm^2

Generation Mode - Two Cell-Stack Units

Emf	29 VOC
Current	50 amps
Calculated efficiency*	37 %
Power	1.1 KW

Storage Mode - One of the Two Cell-Stack Units

Emf	272 VOC
Current	40 amps
Calculated efficiency*	>95 %
Power	11 KW
Capacity	40 KWH

*Includes internal resistance and estimated concentration polarization.

Li/I$_2$ ELECTROCHEMICAL ENGINES INTEGRATED WITH UCC BY THE LASL CONCEPT

The Li/I$_2$ electrochemical engines operate at 625 K and thereby avoid many of the high temperature problems of the proposed new generators mentioned earlier--development and demonstration of such engines should proceed rapidly. As noted earlier and in the Appendix, these Li/I$_2$ electrochemical engines have major advantages for the arid West and elsewhere.

A. They do not require water.
B. They store as well as generate power, thus the generators can be switched as needed to load leveling.
C. They are highly efficient.
D. They are built in small modules. As such they can be replaced easily by electricians in case of malfunction.
E. They offer high reliability because of the large number of units needed in any large operation.

Heat Available for Generation - Consider that we will start with a char from pyrolysis of a Fruitland coal. Pyrolysis at 725 K will have recovered about 22% of the coal's heating value both as fuel gas at about 500 Btu/SCF and as valuable liquid hydrocarbons.

The remaining 78% of the heating value is in char which will be gasified to low Btu fuel. Air combustion of this low-Btu gas will produce hot gas which can deliver about 87% of its heat content at 625 K. This heat is 68% of the total heating value of the coal.

Consistent with discussion in the Appendix the energy conversion of the electrochemical engine is given by (the Carnot efficiency) x (the ratio of real to ideal cell voltage during drain) x (the fraction of the coal's heating value which is found in the char) x (the fraction of the heat of char combustion which is available at 625 K) or

$$\frac{(625-298)}{(625)} \frac{(21)}{(29)} (0.78) (0.87)$$

and about 26% of the coal's energy appears as electrical energy.

The unused heat which an electrochemical engine cannot accept because it is under 625 K can be put underground for preliminary drying. Heat exchangers will not be needed for such drying--just moving the hot gas through the moist coal will be sufficient. Here (0/78)(0.13) or about 10% of the original heat of combustion of the coal could be delivered underground.

For Fruitland coal only about a third of that 10% waste energy could be used for drying coal, but in wetter areas most of the 10% could be used.

Thus the Fruitland coals of arid Northwestern New Mexico, recovered by UCC and utilized by Li/I$_2$ electrochemical engines, could deliver the following percentages of the initial energy of complete combustion:

Electric power output	26%
Hydrocarbon recovery	22%
Preheating	3%
Waste heat	49%

More elaborate heat usage schemes could do even better than 51% utilization, but the estimates in the calculation do not warrant further refinement.

Fig. 4 shows how a community's business and home usage could be filled by keeping electrochemical engines working at all times but gradually switching the engines into and out of storage. This load leveling is important because peak power normally costs roughly three times as much to produce as does baseload. Here there is no need for peak load generators.
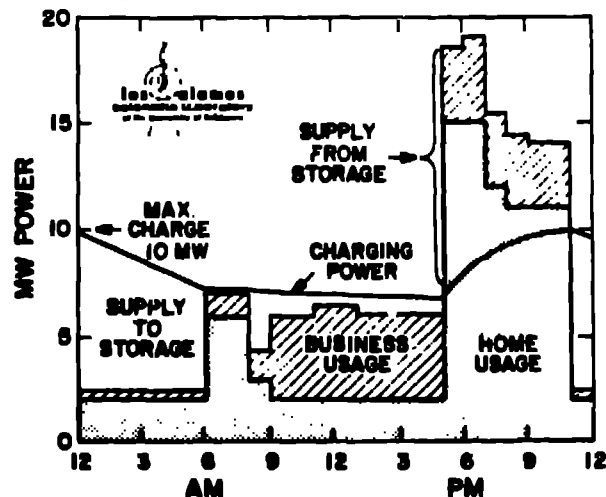

Fig. 4 - Load-leveling by electrochemical engine. (Maximum generation of 10 MW decreases as engines move from generation to storage.

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The corresponding electricity generation efficiency is 0.26/0.66 or 39%. This ~ 39% compares well with the best steam cycle efficiencies noted earlier (~40%) and is better than average steam cycle efficiencies (~33%).

Likewise the present system stores energy for peak periods. Peak generation now is ~20% efficient in the better systems.

Squires (10) has calculated a combined cycle (high-temperature gas turbines plus steam turbines) efficiency of 51% for conversion of delivered coal to electric power. Westinghouse is attempting to develop such turbines plus the high temperature fuel-gas cleanup procedures to be used with them. These systems will not soon be modified for use with UCC systems.

The present Li/I₂ electrochemical engines might usefully be combined with the very high-temperature system mentioned earlier (the gas turbines above, MHD, the sodium heat engine, potassium vapor turbine, etc.), but these developments are not far enough along to warrant combined-cycle calculation yet.

SUMMARY

The UCC-Li/I$_2$ electrochemical engine combination offers very interesting possibilities for electricity generation and hydrocarbon recovery from Southwestern coals.

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APPENDIX - THE EQUILIBRIUM AND DRAIN PERFORMANCE OF LITHIUM/IODINE ELECTROCHEMICAL ENGINES

Thermodynamics - Consider a reaction in which gaseous iodine reacts with molten metallic lithium to produce liquid lithium iodide.

$$2Li_{(1)} + I_{2(g)} = 2LiI_{(1)} \qquad (1)$$
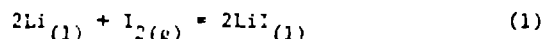
If the reaction takes place in an electrochemical cell, the Gibbs free energy, ΔG, of the process can be extracted as useful electrochemical work. At a temperature where I_2 is the only volatile component this free energy and voltage will be given by

$$\Delta G = -nFE = \Delta G^\circ - RT \ln (f_{I_2}/f^\circ_{I_2})$$

$$= \Delta G^\circ - RT \ln P_{I_2} \qquad (2)$$

where the gas fugacity, f, is assumed equal to its pressure, P, and where the reference fugacities are for 1 atm of iodine and for the condensed phases of the other reactants and products.

Figure 5 shows a schematic drawing of a cell design which has been used in our laboratory studies. In the figure a Pyrex cup with tungsten electrical connector is shown holding three layers of materials. The top layer is a porous graphite disk on which the iodine reacts electrochemically. The middle layer is shown as a zirconia felt pad, but other materials can also be used. This middle layer supports the graphite disk above it, thus providing insulation against electronic short-circuits between the graphite and the nickel felt below. The zirconia felt pad is porous. The lower layer in the Pyrex cup is porous nickel felt which holds the lithium cell reactant. A molten electrolyte containing LiI (plus other salts to lower its melting point) wets into void spaces in all three layers, completely filling the voids in the lower two layers and partially filling the porous graphite by capillary wetting.
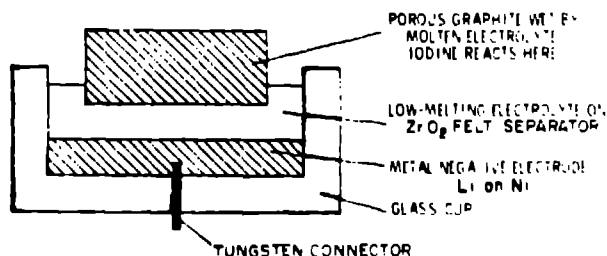

Fig. 5 - Laboratory model of Li/I$_2$ electrochemical engine cell.

Electric power can be supplied by the cell from connections to the lithium-nickel felt-tungsten negative electrode and to the iodine-porous graphite positive electrode. The open circuit (no-drain) voltage of such a cell is calculable from thermodynamic data as in Eq. 2. Values for ΔG° at elevated temperatures are available from the JANAF Tables (9).

For a pressure of 1 atm of I_2 and a cell temperature of 625 F

$$-46,122 \, E_{(1 \, atm)} = -121,800 - 4.575(625)\log 1$$

$$E_{(1 \, atm)} = 2.64 \text{ volts} \qquad (3)$$

For 20 atm which is the vapor pressure of I_2 at 625 K

$$E_{(20 \, atm)} = 2.72 \text{ volts} \qquad (4)$$

and for 0.000405 atm which is the vapor pressure of I_2 at room temperature

$$E_{(0.000405 \, atm)} = 2.43 \text{ volts} \qquad (5)$$

As corollary if two cells are set in electrical opposition, positive-to-positive and negative-to-external load-to-negative, and if both cells are at the same temperature and pressure, e.g., as with Eq. 4 above, then no current will flow and no external work can be done. However, if the pressure in one cell is then changed, e.g., to that in Eq. 5 above, then the two different voltages will not balance. In this case 2.72-2.43 = 0.29 volts applies across the external load, and this voltage is available through a large external load to do work, nEE = (46122)(0.29) calories per mole of iodine reacted in each cell. This work appears at the expense of heat supplied to the system at 625 K.

The Carnot limit of the process appears because the heat of vaporization of iodine must be supplied at 625 K, and the heat of condensation is discharged at 298 K. In terms of temperature the maximum efficiency is

$$eff_{max} = (625-298)/625 = 0.52 \qquad (6)$$

Performance Under Drain - Although the 0.29 volts above is available for infinitely slow drain (one cell discharges while the other cell charges), the voltage for finite electrical drain will always be reduced from this value.

One can speak of the current, I; the external resistance, R_{ext}; and the internal resistance of a draining cell, R_{int}. Then

$$= I(R_{ext} + R_{int}) \qquad (7)$$

For two cells in electrical opposition with the I_2 pressure differences above, and assuming the internal resistance does not differ for discharging and for charging

$$0.29 = I(R_{ext} + 2R_{int}) \qquad (8)$$

In practice we do find very small and constant internal resistances for Li/I_2 electrochemical cells of the type used in electrochemical engines. Specifically, we have measured values as low as 0.8 ohm-cm^2 from 0.25 amps/cm^2 discharge to 0.80 amps/cm^2 charge. Such remarkable behavior could only be found in molten salt systems.

These cells can be stacked into batteries, and a common reservoir can jointly be used for all the cells in each battery. Fig. 6 shows this usage in laboratory electrochemical engines.
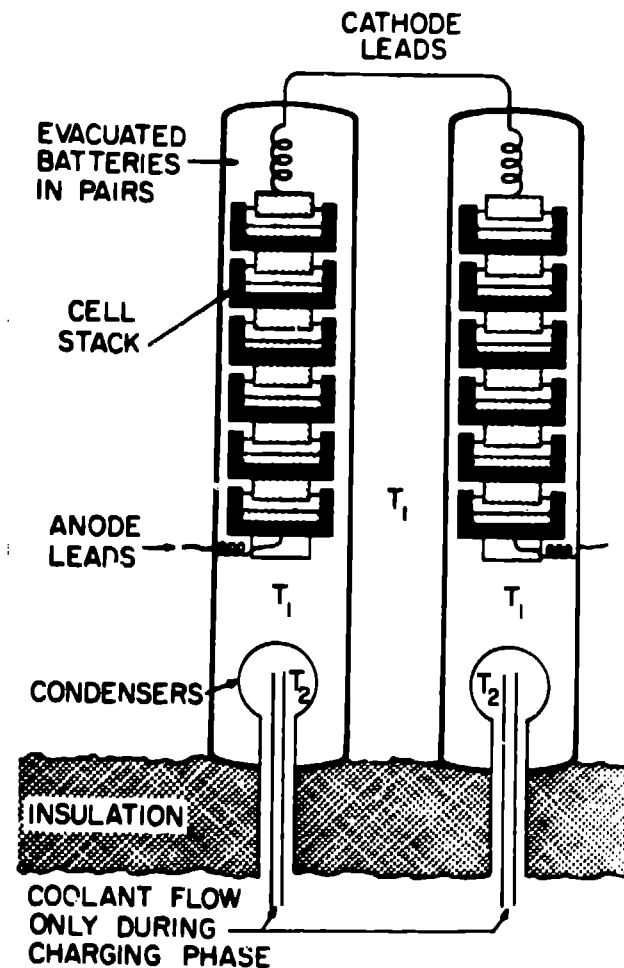

Fig.6 - Laboratory model of Li/I_2 electrochemical engine.

These electrochemical engines do operate consistent with thermodynamic prediction, but this laboratory design does not permit a practical rate of transfer of iodine vapor--for the commercial devices a more open region by the positive electrodes and more direct access to the condenser is necessary.

In the power-generation mode the generation cycle starts with one cell-stack unit fully charged and at uniform temperature (e.g., T_1 = 625 K, condenser T_2 = 298 K on the right). In this half cycle the current flows through both cell-stack units and through an external load across the anode leads, thereby (a) discharging the left cell-stack unit, (b) charging the right cell-stack unit, and (c) doing external work. When the left cell-stack unit is discharged and the right cell-stack unit is charged, then the temperature roles are reversed and the direction of the current is also reversed (requiring an external switching). At the end of this second half cycle the engine has returned to its original condition, and work has been performed at the expense of degradation of heat.

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For storage the cell-stack units are disconnected at the cathode leads (Fig. 6) and $T_1 = T_2$ is maintained throughout. Then each cell-stack unit acts as an independent storage battery. Such batteries have excellent efficiencies and large capacities.

More commercially realistic units are described in the body of this paper.